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(54) Title: MALEIC ANHYDRIDE/ALKYL VINYL ETHER POLYMERIZATION PROCESS (57) Abstract What is described herein is a process for making a copolymer of high specific viscosity by polymerisation of maleic anhydride and a C ₁ -C ₄ alkyl vinyl ether monomer. The invention involves polymerizing said monomers to form a slurry of said copolymer in excess alkyl vinyl ether as solvent and toluene or an aliphatic organic compound as cosolvent, and is characterized by the steps of: (a) precharging a reactor with C ₁ -C ₄ alkyl vinyl ether as solvent at a reaction temperature, (b) feeding a mixture of maleic anhydride and a C ₁ -C ₄ alkyl vinyl ether in substantially stoichiometric amounts, preferably with a slight excess of the alkyl vinyl ether, and at a selected rate, into said precharged reactor, and (c) simultaneously feeding a predetermined mixture of toluene or an aliphatic organic compound and a polymerization initiator continuously over substantially the entire period of polymerization.		

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⁺ It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

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"MALEIC ANHYDRIDE/ALKYL VINYL ETHER POLYMERIZATION PROCESS"

This invention relates to copolymers of maleic anhydride and a C₁-C₄ alkyl vinyl ether, and, more particularly, to a process for making such copolymers of high specific viscosity.

What is described herein is a process for making a copolymer of high specific viscosity by polymerization of maleic anhydride and a C₁-C₄ alkyl vinyl ether monomer. The invention involves polymerizing said monomers to form a slurry of said copolymer in excess alkyl vinyl ether as solvent and toluene or an aliphatic organic compound as cosolvent, and is characterized by the steps of: (a) precharging a reactor with C₁-C₄ alkyl vinyl ether as solvent at a reaction temperature, (b) feeding a mixture of maleic anhydride and a C₁-C₄ alkyl vinyl ether in substantially stoichiometric amounts, preferably with a slight excess of the alkyl vinyl ether, and at a selected rate, into said precharged reactor, and (c) simultaneously feeding a predetermined mixture of toluene or an aliphatic organic compound as cosolvent, and a polymerization initiator continuously over substantially the entire period of polymerization.

In this method, a suitable reactor is provided with appropriate inlet tubes, agitation means, and heater and temperature control means. The reactor is first purged with nitrogen to remove air from the system. Generally three separate purges are employed, at about 3 bars pressure and about 40°C. Then the reactor is precharged with a substantial excess of C₁-C₄ alkyl vinyl ether, preferably methyl vinyl ether, which functions as a solvent to facilitate agitation of the contents of the reactor before and during the polymerization. The alkyl vinyl ether solvent then is heated to a reaction temperature, generally about 50-90°C., and preferably about 60°C.

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Then separate feed tubes carrying molten anhydride and alkyl vinyl ether are combined in a static mixer and fed into the precharged reactor while agitating the solvent. The maleic anhydride and alkyl vinyl ether reactants usually are combined in substantially stoichiometric ratios of about 1:1, although a slight excess of alkyl vinyl ether monomer is preferred in order to assure that all the maleic anhydride reactant will be complexed by the vinyl ether. Suitably a mole ratio of about 1:1.05 to about 1:1.7 is used, although a 1:1.5 mole ratio is preferred.

The combined maleic anhydride-alkyl vinyl ether feed stream is added to the reactor at a substantially constant feed rate over a suitable period of polymerization. Generally, a period of about 3 hours for addition the mixture of both monomers is typical of the process.

The mole ratio of MVE:MA in total present in the reactor during the polymerization suitably is about 3:1 to about 10:1, although lower and higher ratios also may be used. Preferably, a mole ratio of about 8:1 is used.

As a feature of the invention, during substantially the entire period of the polymerization, predetermined amounts of toluene or an aliphatic organic compound as cosolvent and polymerization initiator are introduced continuously into the reactor to control the course of the polymerization. Any suitable initiator known in the art may be used including but not limited to peroxides such as lauryl peroxide. Tertiary-butyl or tertiary-amylperoxy pivalates are preferred. The concentration of initiator may vary widely, but is suitably about 0.05 to 2% by weight of maleic anhydride present, although about 0.1% by weight usually will suffice for carrying out an effective polymerization.

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After the polymerization, the reactor is cooled, excess alkyl vinyl ether (which contains e.g. about 10% toluene) is vented off, and additional toluene is added as a solvent to replace the vented vinyl ether. Then the resultant copolymer slurry in toluene is discharged from the reactor. The copolymer powders can be recovered by filtration and drying. The product is a fine white powder of high specific viscosity with very low residual toluene, generally less than 1%. The copolymer also is quite stable as evidenced by the fact that its viscosity remains substantially constant even after a period of weeks or months.

The vented alkyl vinyl ether-10% toluene mixture can be recycled to function as the precharge in the reactor.

The presence of toluene in the process acts to stabilize the copolymer produced. A suitable amount of toluene for use in the process will produce a reaction slurry mixture at about a 25% solids level after venting alkyl vinyl ether.

The specific viscosities obtained in this process generally range from about 2 to 4, and usually about 3, as determined as a 1% solution in 2-butanone.

Suitable aliphatic organic compounds for use as cosolvents herein include methyl t-butylether, ethyl acetate, butyl acetate, propyl acetate, hexane, heptane and cyclohexane.

The compositions containing copolymers of vinyl alkyl ethers with maleic anhydride, and particularly vinyl methyl ether-maleic anhydride interpolymers generally are stable against changes in viscosity in non-aqueous systems, and particularly when such copolymers are present either in the solid state, in non-aqueous solvent solutions, or in non-aqueous liquid suspensions. Preferably, however, when an aliphatic organic compound is used as cosolvent, stability is enhanced by the addition to or admixture with

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the vinyl alkyl ether-maleic anhydride copolymers of small amounts of free radical inhibiting compounds. Such compounds are characterized as free radical inhibitors and include quinones, hydroquinones, phenols, mercaptans, aromatic amines and aromatic nitro compounds. Butylated hydroxy toluene is a preferred stabilizer compound. The addition of traces of such compounds in amounts of the order of from 0.00001% to 1% based on the weight of the copolymer effects a substantially complete stabilization of the copolymers with which this invention is concerned, whether the latter are present either in the solid state, as a suspension or slurry in a non-aqueous liquid or in a solution in a suitable solvent. The amount of stabilizer which is preferred ranges from about 0.0001% to about 0.1% based on the weight of the copolymer.

The invention will now be described by reference to the following working examples of the invention.

EXAMPLE 1

A reactor equipped with suitable inlet tubes, agitation means, and heater and temperature control means, was purged three times with nitrogen at 3 bars pressure and at 40°C. The purged reactor then was precharged with a recycled mixture of 192.4 g. of methyl vinyl ether containing 19.24 g. of toluene, and heated to 60°C. Then separate streams of 52.5 g. of molten maleic anhydride and 48.0 g. of methyl vinyl ether were combined in a static mixer and introduced into the reactor over a period of 3 hours while agitating the reaction mixture. After 5 minutes, and thereafter simultaneous with addition of monomers, a solution of 128 g. of toluene and 0.066 g. of lauryl peroxide were introduced into the reactor over the 3-hour period of polymerization. The contents of the reactor then were held at 60°C. for 1 hour, cooled to room temperature, and excess methyl vinyl ether was vented.

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Then 100 g. of toluene was added. The resultant slurry was discharged from the reactor, filtered, and the solid obtained was dried. 75 g. (90.2% yield) of the desired copolymer was collected as a fine white powder. The specific viscosity of the copolymer powder was 2.54, determined as a 1% solution in 2-butanone. A triphenylphosphite test was negative showing the substantial absence of residual monomers. The toluene level in the copolymer was only 0.75%. The viscosity of the copolymer was observed to remain substantially constant during a test period of 3 months.

Table 1 below summarizes the experimental conditions of this Example.

TABLE I
SUMMARY OF EXPERIMENTAL CONDITIONS OF EXAMPLE 1

<u>Precharged Reactor</u>				<u>Monomer Feed Composition</u>			<u>Polymerization Period</u>		
Excess MVE (g) (moles)	Toluene (g) (% of MVE)	Temp. (°C.)	MA (g) (mole)	MVE (g) (mole)	Mole Ratio MA:MVE				
192.4	3.3	19.24	10	60	52.5	0.54	47.99	0.83	1:1.5
<u>Toluene and Initiator Feed Composition</u>				<u>Total Addition of</u>					
<u>Toluene</u> (g)	<u>Initiator</u> (g) (% wt.)	<u>Monomer</u> Mole Ratio MVE:MA	<u>Toluene/</u> Initiator — (g)						
128	0.066	0.125	8:1	147.24/0.066	3				

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EXAMPLE 2

A reactor equipped with suitable inlet tubes, agitation means, and heater and temperature control means, is purged three times with nitrogen at 3 bars pressure and at 40°C. The purged reactor then is precharged with a 192.4 g. of methyl vinyl ether and heated to 60°C. Then separate streams of 52.5 g. of molten maleic anhydride and 48.0 g. of methyl vinyl ether are combined in a static mixer and introduced into the reactor over a period of 3 hours while agitating the reaction mixture. After 5 minutes, and thereafter simultaneous with addition of monomers, a solution of 128 g. of methyl t-butylether and 0.066 g. of lauryl peroxide are introduced into the reactor over the 3-hour period of polymerization. The contents of the reactor then are held at 60°C. for 1 hour, cooled to room temperature, and excess methyl vinyl ether vented. Then 100 g. of methyl t-butylether is added. The resultant slurry is discharged from the reactor, filtered, and the solid obtained is dried. 75 g. (90.2% yield) of the desired copolymer was collected as a fine white powder. The specific viscosity of the copolymer powder is about 3, determined as a 1% solution of the copolymer in 2-butanone. A triphenylphosphite test is negative showing the substantial absence of residual monomers.

EXAMPLE 3

The procedure of Example 2 is followed using ethyl acetate, butyl acetate, propyl acetate, hexane, heptane and cyclohexane in place of methyl t-butylether with similar results.

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WHAT IS CLAIMED IS:

1. A process for the production of copolymers of maleic anhydride and C₁-C₄ alkyl vinyl ethers of high specific viscosities characterized by:

(a) precharging a reactor with C₁-C₄ alkyl vinyl ether solvent at a reaction temperature of about 50°-90°C.,

(b) feeding a mixture of maleic anhydride and a C₁-C₄ alkyl vinyl ether in substantially stoichiometric amounts into said precharged reactor at a selected rate,

(c) simultaneously feeding a mixture of toluene or an aliphatic organic compound as cosolvent and a polymerization initiator into the reactor substantially continuously over the period of polymerization, and

(d) copolymerizing said reactants to form a slurry of said copolymer in said solvent and said cosolvent.

2. A process according to claim 1 further characterized by:

(e) venting excess alkyl vinyl ether,

(f) discharging the slurry copolymer product from the reactor, and

(g) recovering the copolymer as a fine, white powder.

3. A process according to claim 1 wherein said cosolvent is toluene.

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4. A process according to claim 1 wherein said cosolvent is an aliphatic organic compound selected from methyl t-butylether, ethyl acetate, butyl acetate, propyl acetate, hexane, heptane and cyclohexane.

5. A process according to claim 1 wherein the mole ratio of alkyl vinyl ether to maleic anhydride in total in the reactor during the polymerization is about 3:1 to about 10:1, respectively.

6. A process according to claim 4 wherein said product includes a stabilizing agent selected from quinones, hydroquinones, phenols, mercaptans, aromatic amines and aromatic nitro compounds.

7. A process according to claim 1 wherein the amount of cosolvent present in the reactor will provide a slurry product at about a 25% solids level after venting alkyl vinyl ether.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/04875

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08F 16/16

U.S. Cl: 526/271

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System

Classification Symbols

U.S. 526/271

Documentation Searched other than Minimum Documentation
to the extent that such documents are included in the fields searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US, A. 4,370,454 (MESSMER et al) 25 JANUARY 1983; See the entire document.	1-7
A	US, A. 3,632,561 (GIBB et al) 04 JANUARY 1972; See the entire document.	1-7
A	US, A. 3,553,183 (FIELD et al) 05 JANUARY 1971; See the entire document.	1-7
A	US, A. 3,532,771 (FIELD et al) 06 OCTOBER 1970; See the entire document.	1-7
A	US, A. 2,782,182 (VERBURG) 19 FEBRUARY 1957; See the entire document.	1-7

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

Date of Mailing of this International Search Report

06 AUGUST 1991

26 AUG 1991

International Searching Authority

Signature of Authorized Officer

ISA/US

Alex H. Walker

3/19/1

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Related WPI Acc No: 1991-237475

XRAM Acc No: C92-037077

Maleic polyanhydride-alkyl polyvinyl polyether copolymer prepn. - by polymerising monomers to form slurry of copolymer in excess polyvinyl ether as solvent and toluene or aliphatic cpd. as co-solvent

Patent Assignee: ISP INVESTMENTS INC (ISPI-N)

Inventor: ARDAN J J; COHEN J M; TAZI M; ZAMORA J N; TAZI M M

Number of Countries: 016 Number of Patents: 006

Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week
WO 9202564	A	19920220				199210 B
EP 542758	A1	19930526	EP 91912312	A	19910711	199321
			WO 91US4875	A	19910711	
JP 5509341	W	19931222	JP 91511821	A	19910711	199405
			WO 91US4875	A	19910711	
EP 542758	A4	19930609	EP 91912312	A	19910000	199526
EP 542758	B1	19951129	EP 91912312	A	19910711	199601
			WO 91US4875	A	19910711	
DE 69115043	E	19960111	DE 615043	A	19910711	199607
			EP 91912312	A	19910711	
			WO 91US4875	A	19910711	

Priority Applications (No Type Date): US 91723991 A 19910701; US 90565002 A 19900809

Cited Patents: US 2782182; US 3532771; US 3553183; US 3632561; US 4370454; DE 1162083

Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
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WO 9202564	A				
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Designated States (National): CA JP

Designated States (Regional): AT BE CH DE DK ES FR GB GR IT LU NL SE

EP 542758	A1	E	10	C08F-016/16	Based on patent WO 9202564
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Designated States (Regional): AT BE CH DE DK ES FR GB GR IT LI LU NL SE

JP 5509341	W		4	C08F-216/18	Based on patent WO 9202564
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EP 542758	B1	E	7	C08F-016/16	Based on patent WO 9202564
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Designated States (Regional): DE FR GB IT

DE 69115043	E			C08F-016/16	Based on patent EP 542758
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Based on patent WO 9202564

Abstract (Basic): WO 9202564 A

Copolymers of high specific viscosity are prepd. from maleic anhydride (MA) and 1-4C alkyl vinyl ethers (AVE) by: (a) precharging a reactor with an (AVE) solvent at a reaction temp. of 50-90 deg.C.; (b) feeding a reaction mixt. of (MA) and (AVE) in stoichiometric amts. into the reactor at a selected rate, (c) simultaneously feeding a mixt. of toluene or an aliphatic organic cpd. as cosolvent and polymerisation initiator into the reactor continuously over the period of polymerisation, and (d) copolymerising the reactants to form a slurry of the copolymer in the solvent and cosolvent.

ADVANTAGE - Copolymers are viscosity stable over a period of weeks or months; solvent and monomer content is very low. (10pp Dwg.No.0/0)

Abstract (Equivalent): EP 542758 B

A process for the production of copolymers of maleic anhydride and

C1-C4 alkyl vinyl ethers characterised by: (a) precharging a reactor with C1-C4 alkyl vinyl ether solvent at a reaction temperature of 50-90 deg.C, (b) feeding a mixture of maleic anhydride and a C1-C4 alkyl vinyl ether in substantially stoichiometric amounts into said precharged reactor at a selected rate, (c) simultaneously feeding a mixture of toluene or an aliphatic organic compound as cosolvent and a polymerization initiator into the reactor substantially continuously over the period of polymerization, and (d) copolymerizing said reactants to form a slurry of said copolymer in said solvent and said cosolvent.

Dwg.0/0

Title Terms: MALEIC; POLYANHYDRIDE; ALKYL; POLYVINYL; POLYETHER; COPOLYMER; PREPARATION; POLYMERISE; MONOMER; FORM; SLURRY; COPOLYMER; EXCESS; POLYVINYL; ETHER; SOLVENT; TOLUENE; ALIPHATIC; COMPOUND; CO; SOLVENT

Index Terms/Additional Words: ETHER

Derwent Class: A14; E14

International Patent Class (Main): C08F-016/16; C08F-216/18

International Patent Class (Additional): C08F-222/06; C08L-029/10

File Segment: CPI

Manual Codes (CPI/A-N): A04-F05; A04-F11; A10-B04; E07-A01; E10-H01E

Chemical Fragment Codes (M3):

01 J011 J271 K0 K9 K910 K930 M210 M214 M215 M225 M231 M233 M262 M272
M281 M282 M320 M416 M620 M781 M782 M903 M904 Q121 R023 9210-G1901-M
9210-G1901-U 9210-G1902-M 9210-G1902-U

02 G010 G100 M210 M211 M240 M281 M320 M414 M510 M520 M531 M540 M610
M781 M782 M903 M904 M910 Q120 Q615 R023 R00862-M R00862-U

Derwent Registry Numbers: 0862-U; 0904-U; 1056-U; 1135-U; 1145-U; 5235-U

Specific Compound Numbers: R00862-M; R00862-U

Generic Compound Numbers: 9210-G1901-M; 9210-G1901-U; 9210-G1902-M;
9210-G1902-U

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